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An Exploration of "The Enumeration of Heterofullerenes"

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This paper introduces fullerenes and heterofullerenes and explains how to enumerate the possible structures of specific patterned heterofullerenes using forms of Burnside's Lemma, Pólya's Theorem, and the generalized character cycle index (GCCI) in reference to "The Enumeration of heterofullerenes" by Zhang et al. Note all generic formulas are highlighted in blue and all formulas specific to an example or to heterofullerenes are highlighted in green.

1. A Brief Explanation of Fullerenes and Heterofullerenes

Fullerenes, discovered in 1985, are spherical, ellipsoidal, or tubular shaped hollow carbon structures. Spherical fullerenes consist of 60 carbon atoms arranged in a hollow sphere with hexagonal and pentagonal bonds. Ellipsoidal fullerenes are made up of 70 carbon atoms with hexagonal bonds only. Fullerenes that form in a tube shape are called carbon nanotubes and are used in a variety of ways, from reinforcing materials to being used as a container to transport drugs that are harmful to human cells to a tumor. Some scientists have also studied fullerene-like molecules, which are made up of elements other than carbon. For example, discovered in 1992, tungsten disulfide can form a fullerene-like structure. When its planar form is folded, it stabilizes into a spherical, hollowed-out structure.

Heterofullerenes were first discovered in the 1990s when scientists found that replacing some atoms of carbon in a spherical fullerene was possible and could lead to a variety of useful molecules with various properties. Two of the most common elements used in this replacement are boron and nitrogen. One reason to use these two elements is that nitrogen, boron, and carbon atoms are similar in size so replacing these atoms in the fullerene allows it to retain its shape and electron structure. These atoms, which are doped (substituted) into the spherical carbon fullerene, are called heteroatoms, hence the name heterofullerenes. Since this discovery,

scientists have wanted to enumerate the possibilities of heterofullerenes to theoretically determine the number of positional and chiral isomers for a compound.

2. The Enumeration of Heterofullerenes

A graph consists of two sets: one of vertices and the other of edges. In a molecular graph, the atoms are represented by vertices and the bonds are the set of edges. Any hydrogen atoms may be omitted from this graph. A spherical fullerene can be represented as a connected graph with order 60. All of the vertices in this graph are carbon atoms. The most well-known fullerene is formed by 20 hexagonal and 12 pentagonal faces. According to Ashrafi et al. in chapter 16 of their book, *Topological Modeling of Nanostructures and Extended Systems*, the number of edges (bonds) in a fullerene graph is

$$q = \frac{5p+6h}{2} = \frac{3n}{2}.$$

Note that p is the number of pentagonal faces, h is the number of hexagonal faces, and n is the number of vertices (atoms) in the fullerene. So, for the aforementioned fullerene, C_{60}, with p = 12 and h = 20,

$$q = \frac{5*12+6*20}{2} = \frac{3*60}{2} = 90.$$

Now consider a heterofullerene, which has the same number of edges, q, and the same number of vertices, n. However, one or more of these vertices are replaced with heteroatoms such as boron or nitrogen. This can be depicted by assigning a color to each heteroatom and coloring the substituted vertices with the color that represents its replacement atom. Isomers are molecules with the same formula that have different structural arrangements of their atoms. To enumerate the possibilities of different heterofullerene structures, called isomers, the symmetries of the representative graphs must be calculated. Chirality is one symmetric property of molecular graphs. Isomers are said to be chiral when they have the same atoms and connections but are not

superimposable. A chiral center is found at the position of an atom whose connections are causing chirality. The number of possible chiral isomers is 2^t where t is the number of chiral centers a molecule has. Chirality only exists when no improper rotations, improper axis, centers of inversion, or mirror planes are present in the molecule.

There are two groups that must be considered for the enumeration of heterofullerene structures, the rotation group and the whole automorphism group, or point group, which includes the rotation group and the improper rotation group. The rotational group for C_{60} is called the icosahedral group, denoted I_k. It is made up of the number of different positional isomers and chiral isomers. In the paper "The Enumeration of heterofullerenes", by Zhang et al., I_k is calculated using Pólya's Theorem and its generalization.

The Generic Cycle Index

Note: All g ∈ G can be uniquely written as a product of disjoint cycles. The image of i under the permutation g is gi. With $1 \leq k \leq n$, let $j_k(g)$ be the number of i of length k in g. The generic cycle index formula is given:

$$Z_G(z_1, z_2, \ldots, z_n) = \frac{1}{|G|} \sum_{g \in G} z_1^{j_1(g)} z_2^{j_2(g)} \ldots z_n^{j_n(g)})$$

For a heterofullerene, I (the identity element), C_2: π-rotation, C_3: $\frac{2}{3}\pi$-rotation, and C_5: $\frac{2}{5}\pi$-rotation are the rotation types for I_k. In the calculation of rotations, the identity element (I) is a product of 60 length1-cycles, contains 1 element, and has cycle index notation z_1^{60}. C_2 is a product of 30 length 2-cycles, has 15 elements, and is denoted z_2^{30}. C_3 is a product of 20 length 3-cycles, has 20 elements, and is denoted z_3^{20}. C_5 is a product of 12 length 5-cycles, has 24 elements, and is denoted z_5^{12}. Therefore the cycle index for I_k is:

$$Z_G(z_1, z_2, \ldots, z_n) = \frac{1}{60}(z_1^{60} + 15\, z_2^{30} + 20\, z_3^{20} + 24\, z_5^{12})$$

The cycle index above calculates the rotation group for a heterofullerene. Next we will look at the automorphism group (S_n), or point group, which includes proper and improper rotations. The point group of C_{60}, $S_n = \{I_k, PI_k\}$, where PI_k, representing the improper rotations of the fullerene, is I_k multiplied with the inversion operator (P).

General Form of GCCI

Note: All g ∈ G can be uniquely written as a product of disjoint cycles. The image of i under the permutation g is gi. With $1 \leq k \leq n$, let $j_k(g)$ be the number of i of length k in g.

$$P_G^X(z_1, z_2, z_3, \ldots, z_n) = \frac{1}{|G|} \sum_{g \epsilon G} [\, X(g) \prod_{k=1}^{n} z_k^{jk(g)} \,]$$

The linear character of the irreducible representation of G, denoted X(g), is 1 for a proper rotation and -1 for an improper rotation.

In the calculation of improper rotations, R_0 = PI has 1 element and is denoted z_2^{30}. $R_1 = PC_2$ has 15 elements and is denoted $z_1^4 z_2^{28}$. $R_2 = PC_3$ has 20 elements and is denoted z_6^{10}. $R_3 = PC_5$ has 24 elements and is denoted z_{10}^6. The terms from the cycle index of rotations and the terms R_0, R_1, R_2, and R_3 create the generalized character cycle index (GCCI).

GCCI for S_n of C_{60} the antisymmetric representation:

$$P_G^X(z_1, z_2, z_3, \ldots, z_n) = \frac{1}{120}(z_1^{60} + 15z_2^{30} + 20z_3^{20} + 24z_5^{12} - z_2^{30} - 15z_1^4 z_2^{28} - 20z_6^{10} - 24z_{10}^6)$$

Simplified $P_G^X(z_1, \ldots, z_n) = \frac{1}{120}(z_1^{60} + 14z_2^{30} + 20z_3^{20} - 15z_1^4 z_2^{28} + 24z_5^{12} - 20z_6^{10} - 24z_{10}^6)$

Note: There exists another representation of the S_n, the point group, of C_{60} where X(g) is always one. This changes the GCCI by adding $2z_2^{30}$ leading to a GCCI:

$$P_G^X(z_1, \ldots, z_n) = \frac{1}{120}(z_1^{60} + 16z_2^{30} + 20z_3^{20} - 15z_1^4 z_2^{28} + 24z_5^{12} - 20z_6^{10} - 24z_{10}^6)$$

Now let A denote the set of vertices in the graph of C_{60} (all carbon). Let C = {c_1, c_2,…, c_m) be the set of all possible elements of the heteroatoms to be substituted into the fullerene. Let m = |C|. The enumeration is simply the coloring of one or more vertices in A by C, in other words replacing a carbon with a heteroatom. Note: C^A is a mapping from A to C.

Zhang et al.'s version of Pólya's Theorem

Let F be the set of all orbits of (G, C^A). Then: |F| = Z_G(m, m,…, m).

The number of positional isomers is the number of different orbits of I_k (icosahedral group) acting on A^C, so the cycle index of the icosahedral group substituting m for every z is:

$$Z_G(m, m,\ldots, m) = \frac{1}{60}(m^{60} + 15m^{30} + 20m^{20} + 24m^{12}).$$

Now, consider a specific pattern of heteroatoms being inserted into the fullerene. Let k_i be the number of c_i elements (number of heteroatoms), where I = 1, 2,…, m. And let the pattern for a the chemical formula for a specific heterofullerene be (k_1, k_2, k_3,…, k_m). In other words let each k_i represent the number of each atom of distinct elements in the heterofullerene. The number of distinct positional isomers is equal to the coefficient of (k_1, k_2, k_3,…, k_m) in the following expression:

$$Z_G\left(\sum_{i=1\ldots m} x_i, \sum_{i=1\ldots m} x_i^2, \ldots, \sum_{i=1\ldots m} x_i^n\right)$$

$$=\left(\left(\sum_{i=1\ldots m} x_i,\right)^{60} + 15\left(\sum_{i=1\ldots m} x_i^2\right)m^{30} + 20\left(\sum_{i=1\ldots m} x_i^3\right)^{20} + 24\left(\sum_{i=1\ldots m} x_i^4\right)^{12}\right).$$

The coefficient is denoted $N(k_1 + k_2 + k_3 + \ldots + k_m) = \frac{1}{60}\sum_{i=1\ldots m}|\mathrm{Fix}(g)|$,

Fix(g) is the set of fixed points of g.

Consider counting the number of distinct chiral isomers of C_{60} by applying $\sum_{i=1\ldots m} x_i$, $\sum_{i=1\ldots m} x_i^2$,…, $\sum_{i=1\ldots m} x_i^n$ to the GCCI:

$$P_G^X\left(\sum_{i=1\ldots m} x_i, \sum_{i=1\ldots m} x_i^2, \ldots, \sum_{i=1\ldots m} x_i^n\right)$$

$$= \frac{1}{120}((\sum_{i=1\ldots m} x_i)^{60} + 14(\sum_{i=1\ldots m} x_i^2)^{30} + 20(\sum_{i=1\ldots m} x_i^3)^{20} + 24(\sum_{i=1\ldots m} x_i^5)^{12} -$$

$$15(\sum_{i=1\ldots m} x_i)^4(\sum_{i=1\ldots m} x_i^2)^{28} - 20(\sum_{i=1\ldots m} x_i^6)^{10} - 24(\sum_{i=1\ldots m} x_i^{10})^6)$$

The coefficient of this will be $N(k_1 + k_2 + k_3 + \ldots + k_m) = \frac{1}{120}\sum_{i=1\ldots m} |\text{Fix}(g)|$.

The number of orbits under its entire automorphism group, P_{Sn}^1 is equal to the difference between the number of distinct positional isomers and the number of distinct chiral isomers giving us:

$$P_{Sn}^1 = Z_{Ik} - P_{Sn}^x.$$

This method will find the number of possible structures for a specific patterned heterofullerene.

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